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PROCESS FOR PURIFICATION OF SOLIDS

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H. Herzer, H. J. Rath and D. Schmidt

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Applicant: Wacker-Chemitronic Company for Basic Electronic  
Materials, mbH, 8263 Burghausen

Inventor: Herzer, Heinz, graduate physicist, Dr.  
Rath, Heinz-Jörg, graduate chemist, Dr.  
Schmidt, Dietrich, graduate physicist, Dr.  
8263 Burghausen.

Fig. 1

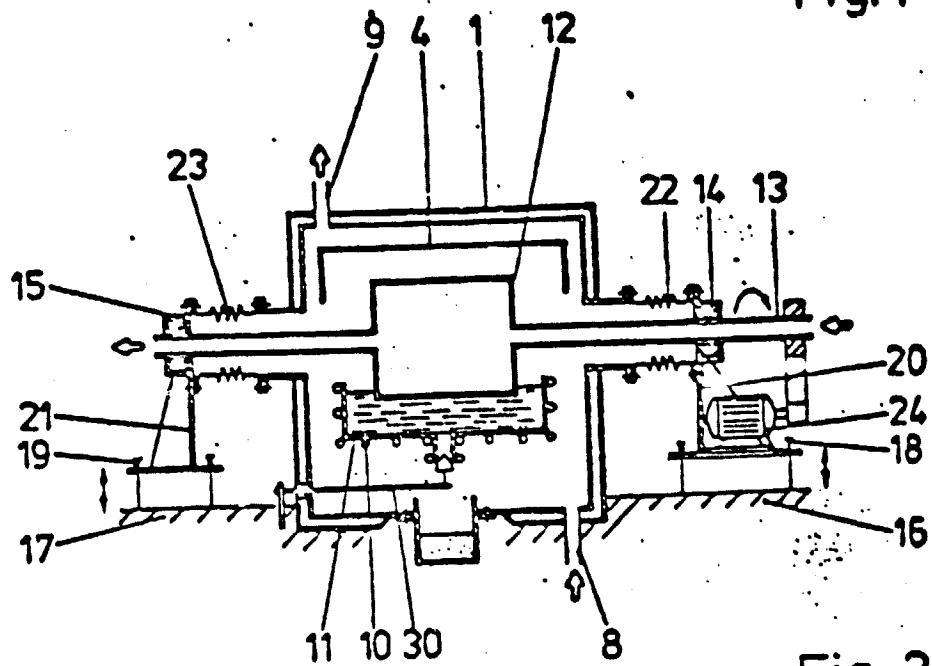
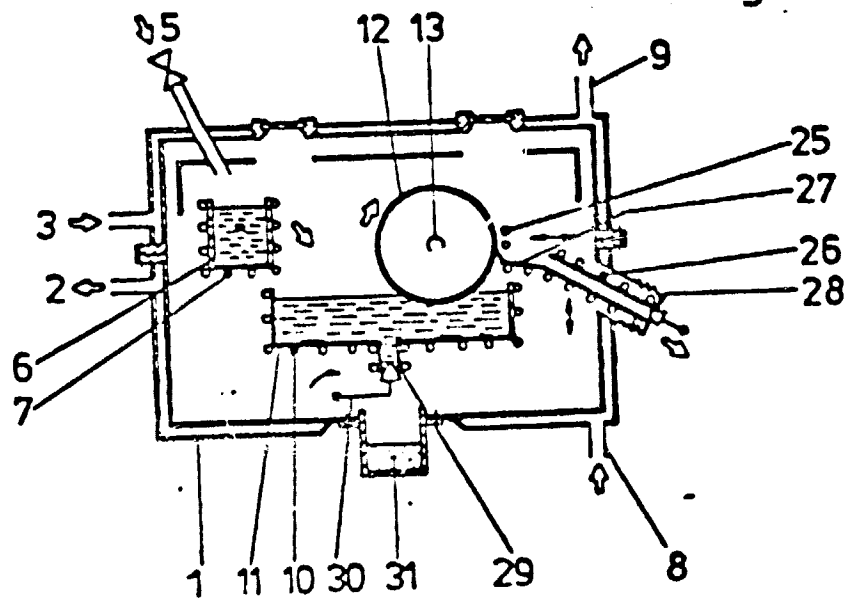


Fig. 2



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PROCESS FOR PURIFICATION OF SOLIDS

Patent Claims:

1. Process for purification of solids by fusion and subsequent solidification, characterized by the fact that a rotating roller made of material resistant to the fused solid and cooled below the melting point of the solid to be purified is immersed in the melted solid, and the fact that the resolidified solid adhering to the roller passes through a subsequent zone of higher temperature, above the melting point of the solid to be purified, in which the solid adhering to the roller is remelted and collected in a suitable device.
2. Process as in Claim 1, characterized by the fact that the depth of immersion of the roller is adjusted to 0.1 to 0.2 times the roller diameter.
3. Process as in Claims 1 and 2, characterized by the fact that the residence time of the roller surface immersed in the melt of the solid to be purified, expressed in minutes, is 0.005 to 0.25 times the numerical value of the roller diameter.
4. Process as in Claims 1 to 3, characterized by the fact that the solid resolidified on the roller is remelted before it is reimmersed, at a distance from the melt surface of  $0.1 \text{ to } 0.5 \pi d$ , measured on the roller circumference where  $d$  is the roller diameter, and is collected in a suitable device.

5. Process as in Claims 1 to 4, characterized by the fact that the roller is internally cooled.
6. Process as in Claims 1 to 5, characterized by the fact that the roller is cooled by a cooling gas flowing through the interior of the roller.
7. Process as in one or more of Claims 1 to 6, characterized by the fact that semiconductor materials are purified.
8. Process as in Claim 7, characterized by the fact that silicon is purified.
9. Process as in Claim 8, characterized by the fact that the silicon melt is held at a temperature of 1430° to 1500°C.
10. Process as in Claim 7 and one or more of Claims 1 to 9, characterized by the fact that the roller is cooled internally to a temperature of 800° to 1200°C.

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The object of the invention is a process for purifying solids, especially silicon, by melting and subsequent resolidification.

In discussions of energy in recent years, generation of electrical power by direct conversion of solar energy into electrical energy has become increasingly important. But, in order to make silicon solar cells, for instance, economically competitive, it is essential to make a substantial reduction in the cost of the raw material of required purity, which exists on the earth in essentially unexhaustable quantity. Gas phase purification, such as is standard today in production of silicon for the electronic industry, is immediately ruled out because such a process is too energy-intensive and, therefore, too

expensive by a considerable factor. In addition, the purity requirements for silicon to be used in solar cells are not as great as those for 'wafer silicon' to be used in production of expensive components.

To be sure, it is known from Swiss Patent No. 567 435 that technical grade silicon can be purified by leaching with hydrochloric acid; but this process is extremely slow and gives as the result a silicon which without further purification is useful at best as an alloying component, and is not useful as a raw material for production of electronic components or solar cells. Purer silicon is also not obtainable from the known process of gas blowing. With this process, as described in German Patent 10 39 752, silicon is purified by blowing chlorine into the melt.

The object of the invention, then, was to find a process of purifying silicon which gives a purer product than the processes discussed above, and, at the same time, considerably lower costs than the purification process based on decomposing gaseous silicon compounds.

This problem was solved by a process which is not limited only to silicon, but is generally applicable in purification of solids, and which is characterized by the fact that a roller of material inert to the solid to be purified is immersed and rotated in the fused solid; the roller is cooled below the melting point of the solid to be purified, and material which adheres to the roller and solidifies on it passes through a subsequent zone of higher temperature, above the melting point of the solid being purified, so that the material solidified on the roller is again melted and collected in a suitable device.

The parameters influencing crystal growth are adjusted so as to yield a crystallization velocity perpendicular to the



surface of 0.01 to 2 cm per minute, and preferably 0.2 to 1 cm per minute. These parameters include the depth of roller immersion; the rate at which a point on the roller surface moves through the melt; the temperature of the melt of the solid being purified, and the temperature of the roller. One attempts to get a layer thickness for material adhering to the roller surface of 0.005 to 0.05 times the roller diameter, and preferably 0.01 to 0.02 times the roller diameter.

The required immersion depth for the roller in the melt is adjusted to 0.01 to 0.3 times the roller diameter, and preferably to 0.1 to 0.2 times the roller diameter.

The rate of roller rotation is established so that the residence time of the roller surface in the melt of the material to be purified, measured in minutes, is 0.0025 to 0.5 times the roller diameter, and preferably 0.005 to 0.25 times the numerical value of the roller diameter. The temperature of the melt should not be more than 400° above the melting point of the solid to be purified.

As a rule, good results are achieved, especially for low-melting materials, with melt temperatures which are 20° to 100° above the melting point. For the preferred raw material, silicon, for instance, a silicon melt temperature of 1430° to 1500° has proved good.

The melt can be heated by the usual methods, for instance, by resistance heating, radiant heating, or, in case of silicon, by suitable induction heating.

The temperature of the roller turning through the melt is, of course, dependent on the established melt temperature. If the melt temperature is very high above the melting point of the solid to be purified, then in general the temperature of the roller must be very low; that is, far below the melting point of the solid being purified, so that crystallization

will occur on the roller as it passes through the melt. That is, if the melt temperature is, for instance,  $400^{\circ}$  above the melting point of the solid to be purified, then the roller must be at a temperature at least  $400^{\circ}$  to  $800^{\circ}$  below the melting point of the solid. With the preferred embodiment of the process, as already mentioned, one can conveniently set the temperature of the melt relatively close above the melting point of the solid, so that the roller temperature need not be so far below the melting point of the solid. In the purification of silicon, the silicon melt is, as already stated, held at a temperature of  $1430^{\circ}$  to  $1500^{\circ}$ , so that the recommended roller temperature is from  $800^{\circ}$  to  $1200^{\circ}$ , measured at the internal surface of the roller with a cooling agent flowing through it. The stated temperature ranges should be understood as average temperatures, as the part of the roller immersed in the melt will certainly be hotter than the part above it, which has already been out of the melt for some time.

For cooling, a cooling medium flows through the interior of the roller. The cooling medium is adjusted to give the desired temperature. Thus, if one must purify solids with low melting points, so that cooling temperatures below  $100^{\circ}$  must be maintained, then, for instance, a liquid coolant could be used. For still lower temperatures, a liquefied gas could be used. For the preferred application of the process to silicon, it has proved good to use gaseous coolants flowing through the cooling roll, especially nitrogen or argon.

In general, the material in which the solid to be purified is melted must be inert to that solid; that is, it must not cause added contamination of the solid. In the case of silicon, for instance quartz and especially vitreous carbon are suitable. The requirements for the crucible material also apply for the roller to be used. There is the added requirement for the rollers that the roller must be wetted by the material being purified; otherwise, no material would adhere to the

roller. For purification of semiconductors, especially silicon, vitreous carbon has proved to be a very good roller material.

The effective segregation coefficients of the impurities considered are decisive for the purification action. After the roller has continuously removed purified solid, such as purified silicon, the remaining impurities are enriched in the melt. The purification effect can be increased, for instance, if the crucible is rotated, or a stirrer is used to move the melt, or, for instance, even a gas is introduced, causing turbulence and better mixing in the melt. If one wishes to run the process continuously, the crucible can be repeatedly recharged with silicon while the melt, enriched with contaminants, is continuously or at intervals removed from below. The highly impure melt can then be prepurified by known methods, outside the containers, for instance, by leaching with acids, before it is recharged into the crucible.

The resolidified coating of material adhering to the roller (the crystalline silicon film, for instance) is removed in this manner: The adhering solid material is remelted before it is reimmersed, at a distance above the melt surface which is preferably  $0.2$  to  $0.5 \pi d$ , measured along the roller circumference, where  $d$  is the roller diameter. The adhering solid, crystallized silicon for example, is melted again by a water-cooled high-frequency cutting bar running the length of the roller, such as a single-turn copper or silver coil touching the silicon adhering to the roller. Other possibilities for melting the silicon could be attained using suitable laser radiation focused by a concave mirror or, if the process is carried out in high vacuum, with an oscillating electron beam.

The solid, melted in one way or another, drops under the influence of gravity over a scraper, away from the roller and is collected in a suitable device, e. g., a melt trough, and is lead out of the reactor. The melt of purified solid which is drawn off can then, for instance, be taken directly

to a second purification system. By setting up several such systems in series, the purification action can be increased considerably.

The efficiency of the purification process depends generally on the effective segregation coefficients (distribution coefficients). The effective segregation coefficient differs from the theoretical segregation coefficient because it takes into consideration factors such as the mixing of the melt, the crystallization velocity, and the crystallite size.

The process is generally applicable at pressures from  $10^{-9}$  to 2 bar. Operation under vacuum is preferred because of the purification effect due to volatilization of impurities, depending on their particular volatilization coefficients.

The process is particularly suited for purifying metals and especially semiconductor materials such as germanium and silicon. It is no doubt of greatest importance for purification of silicon, which will certainly have to be available in large quantities in the near future for production of solar cells. As the purifying action of the process described depends on the segregation coefficients of the impurities, a contaminant like boron, with a distribution coefficient of about 0.8 can practically not be removed from silicon. This is not important because silicon has to be p-dosed for production of solar cells anyway, so that boron-dosed silicon is used.

The process of the invention will be explained using the figures. Figure 1 shows a system schematically from the side, in section. Such a system would be suitable for carrying out the process of the invention. Figure 2 shows the same system in section from the front.

The steel reactor 1 has a double-walled jacket through which water can flow from connections 2 and 3. It has an internal radiation reflector 4 of molybdenum plate.

The reactor is charged through the closable tube 5 with 120 kg silicon having an iron content of 10 ppm. The charge is placed into a vitreous carbon crucible, 6, having a volume of  $0.04 \text{ m}^3$ , which is heated with a resistance heater 7, under argon. Before melting, the air in the reactor was flushed out with argon flowing in from inlet 8, with outlet 9 open. Then the fused silicon is poured, by tilting the crucible 6, into the vitreous carbon crucible 11 which is underneath. The crucible 6 is recharged with silicon through the filling tube 5. Crucible 11 has a length of 70 cm, a width of 50 cm, and a height of 20 cm. Then a hollow vitreous carbon roller 12 is immersed 4 cm into the melt surface. The roller, with an outside diameter of 30 cm and a length of 50 cm with a wall thickness of 0.4 cm, is mounted by the hollow shaft 13 at both ends of the roller long axis. The shaft is held in graphite-lubricated bearings in mounts 14 and 15. The distance of the mounts 14 and 15 from the floor, 16 and 17, can be adjusted by adjusting screws 18 and 19 on the stand, 20, 21. This makes it possible to lower the roller 12 into the melt, along with its mounts, 14 and 15, by means of the gas-tight stainless steel bellows 22 and 23. The roller 12 was then driven through a gear drive, by the electric motor 24, at 9.5 rotations per minute, corresponding to a peripheral speed of 14.25 cm/minute for any point on the surface. During this, argon at about  $25^\circ\text{C}$  is passed through the hollow shaft at a rate of 2 standard cubic meters per hour, giving a mean temperature of about  $1000^\circ\text{C}$  for the inside surface of the roller. For a crystallization velocity of about 0.4 cm per minute perpendicular to the surface, the silicon layer at the surface of the roller had grown to about 0.6 cm thick when it emerged from the melt. After moving about  $220^\circ$  after emerging from the melt, at about 15 cm before reimmersion (measured along the roller surface), the adhering silicon layer was remelted by the one-turn water-cooled copper induction coil 25, so that liquid silicon dropped off. The liquid silicon was passed out of the reactor through the outlet trough 27, which was heated above the melting point of silicon by the resistance

heater 26. The sidearm 28 which takes up the silicon flow could, if desired, be connected to an argon-covered silicon collector vessel; or it could be connected to the filler tube, 5, of a second similar purification system. Only one purification step was carried out with the example depicted here, though. That is, the silicon was collected and its purity was determined. For a take-off of 59 kg purified material per hour, the process was terminated after 48 hours. At hourly intervals during this period, 4 kg of melt enriched with impurities was drained off through the outlet pipe 29 in the bottom of crucible 11, by actuating lever 30. This was drained into the vessel 31, of vitreous carbon, which could be unscrewed. The 190 kg of residual melt collected during 48 hours was pre-purified by leaching with hydrochloric acid and added to the silicon of a new charge. The 2,832 kg purified silicon obtained in the same period had an iron content of only 10 ppb by weight. The decrease in the other impurities was correspondingly extensive except for boron and, to a limited extent, phosphorus. The p-conducting silicon thus obtained could immediately be cast into appropriate plates for production of solar cells.